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1. Title of Invention

Method for peroxide bleaching of wood pulp

2. Scope of Demand for Patent

(1) A method of bleaching wood pulp characterized in that following peracetic acid bleaching of wood pulp using a solution of peracetic acid containing hydrogen peroxide, the residual hydrogen peroxide is activated with an alkali and hydrogen peroxide bleaching is performed in a sequence.

(2) A method of bleaching wood pulp as claimed in claim 1 wherein said peracetic acid bleaching is performed following treatment of wood pulp with an acid, a chelating agent or a phosphate salt.

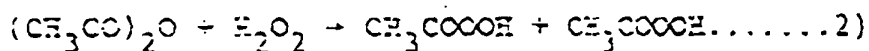
3. Detailed Description of the Invention

This invention relates to a peroxide bleaching method for wood pulp. More particularly, the invention

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relates to a method for improving the effect of bleaching, characterized in that following peracetic acid bleaching, the residual hydrogen peroxide is treated with an alkali and hydrogen peroxide bleaching is performed in a sequence.

While peracetic acid is produced by auto-oxidation of acetaldehyde or acetylation of hydrogen peroxide, the product obtained by the latter method is generally used for bleaching purposes. According to this production technology, hydrogen peroxide is reacted with either glacial acetic acid or acetic anhydride under conditions acidic to sulfuric acid and the respective reactions can be written as follows.



The product according to reaction schema 1) is known as equilibrium peracetic acid and the product is commercially available as industrial grade peracetic acid. Its typical composition is 42% peracetic acid, 6% hydrogen peroxide, 37% acetic acid, 14% water and 1% sulfuric acid.

The process according to reaction schema 2) is known as the in situ process, by which peracetic acid can be easily produced from hydrogen peroxide of low concentration and acetic anhydride even in a peracetic

acid-consuming plant, such as a pulp plant. The product typically contains 23% peracetic acid and 8% hydrogen peroxide.

While both of these grades of peracetic acid can be used in the bleaching of pulp, the peracetic acid solution produced in either case contains hydrogen peroxide.

Though it depends on the type of substrate pulp and the quality requirements, the bleaching of wood pulp with such peracetic acid is generally performed under the conditions of pH 2-8, pulp concentration 8-15%, temperature 40-80°C and bleaching time 1-3 hours.

Peracetic acid bleaching has been explored for the bleaching of a variety of pulps. In the bleaching of mechanical pulp, satisfactory bleaching effects with minimal decreases in bleaching yield have been attained. As inferable from the fact that it has been used as an adjusting agent in the extraction of holocellulose from wood, peracetic acid does not damage carbohydrates and has a high delignification power. Therefore, it has for some time been a subject of research for possible application to the bleaching of chemical pulp. Particularly in view of the recent demand for environmental protection, a switchover from chlorine type bleaching to oxygen type bleaching is being

explored for preventing pollution due to bleach effluents. Under the circumstances the excellent delignification and bleaching powers of peracetic acid are attracting attention.

For example, Japanese Patent Publication No. 11402/1979 proposed a three-stage bleaching process called D-PA-D (D = chlorine dioxide bleaching and PA = peracetic acid bleaching) as a method of bleaching kraft pulp dispensing with chlorine bleaching for avoiding the risk of toxic effects of chlorine-bleach waste water on fish. According to the same patent literature, bleaching to a degree of brightness over 80% is possible without detracting from yield and pulp viscosity.

There has also been introduced, as exclusively oxygen type bleaching processes with an interposition of peracetic acid bleaching, the O-PA-P (O = oxygen bleaching and P = hydrogen peroxide bleaching) 3-stage process and the P-PA-P 3-stage process which do not liberate chloride ion in the bleach waste water and in which the waste water can be reused and ultimately concentrated and combusted in a recovery furnace.

Thus, peracetic acid bleaching has attracted attention as a unique oxygen type bleaching technology but it is still in the research stage and has not been

implemented on an industrial scale as yet. This is because peracetic acid is too expensive for use as a bleaching chemical and any bleaching process involving peracetic acid bleaching is economically handicapped.

For the purpose of reducing the peracetic acid bleaching cost and improving the economics of the process, the present inventors studied the composition of the peracetic acid solution obtainable by acetylation of hydrogen peroxide and explored into a technology for utilizing all the peroxide available to advantage and thereby enhancing the effect of bleaching. The investigation culminated in the present invention.

This invention is, therefore, concerned with a method of bleaching wood pulp characterized in that following peracetic acid bleaching using a solution of peracetic acid containing hydrogen peroxide, the residual hydrogen peroxide is activated with an alkali and hydrogen peroxide bleaching is performed in a sequence.

The method of the invention is now described in further detail. Peracetic acid bleaching is performed using the peracetic acid synthesized by acetylating hydrogen peroxide and containing hydrogen peroxide. The level of addition based on bone-dry pulp is generally about 0.2 to 10% as peracetic acid according to the

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required brightness and quality. This bleaching is carried out under the conditions of pH generally 2-8 and preferably 4-6, pulp concentration generally 5-20% and preferably 10-15%, temperature generally 20-100°C and preferably 40-80°C, and bleaching time generally 30 min-4 hrs and preferably 1-2 hrs. In order to inhibit decomposition of peracetic acid and hydrogen peroxide by the heavy metal catalyst, it is preferable to employ a polyphosphate such as sodium tripolyphosphate or an aminopolycarboxylate such as EDTA (ethylenediamine-tetracetate) in conjunction.

The pulp having gone through peracetic acid bleaching under the above conditions is not washed but mixed with an alkali for activation of residual hydrogen peroxide and immediately subjected to hydrogen peroxide bleaching. The amount of the alkali is generally about 0.5 to 2% based on bone-dry pulp, or sufficient to adjust the pulp slurry to pH 9-11. The bleaching temperature is 20-100°C and preferably 40-80°C and the pulp concentration is 5-20% and preferably 10-15%. The bleaching time is generally 30 min. to 3 hrs. and preferably 30 min. to 2 hrs.


When the alkali is added, hydrogen peroxide may be additionally supplied, where necessary, whereby a higher degree of brightness is obtained at this bleach-

ing state.

The above bleaching process ends with final rinse but when a still higher degree of brightness is required, the bleaching process may be repeated.

The alkali which can be employed for purposes of this invention includes, among others, hydroxides of alkali metals such as sodium, potassium, etc., hydroxides of alkaline earth metals such as calcium, magnesium etc., sodium carbonate, ammonium carbonate, sodium phosphate, ammonia and so on.

In order to obviate decomposition of peracetic acid and hydrogen peroxide by heavy metal, the pulp prior to peracetic acid bleaching may be treated with an acid, an organic chelating agent, a phosphate salt or the like, whereby the brightness of bleached pulp is further improved. Specifically, prior to peracetic acid bleaching, the pulp is generally diluted to a concentration of 1-5% and, in the case of acid treatment, adjusted to pH 1-5 with a mineral acid such as sulfuric acid, hydrochloric acid, etc. or an organic acid such as acetic acid, formic acid, etc. After a certain time, the pulp is dehydrated and after removal of heavy metals, subjected to peracetic acid bleaching. In the case of an organic chelating agent, EDTA, NTA (nitrilotriacetate), DTPA (diethylenetriaminepent-



acetate) or the like is added in a proportion of 0.05-0.5% and a similar treatment is carried out at pH 5-9. In the case of phosphoric salt treatment, sodium metaphosphate, sodium tripolyphosphate, sodium pyrophosphate or the like is added in a proportion of 0.5-3% and a similar treatment is carried out at pH 7-9.

The method of this invention can be applied to any type of pulp such as chemical pulp, semi-chemical pulp or mechanical pulp, only provided that treating conditions are properly adjusted.

The advantage of this invention using peracetic acid is that compared with the conventional technology, a higher degree of brightness can be attained at reduced cost and without a compromise in the quality of bleached pulp. Firstly, hydrogen peroxide occurring as an impurity in peracetic acid can be effectively utilized for bleaching to enhance the effect of bleaching, thus contributing to reduction of bleaching cost. Secondly, because the impurity peracetic acid can be effectively utilized, the rate of conversion from hydrogen peroxide to peracetic acid in the equilibrium or in situ production of peracetic acid need not be critically controlled and, therefore, the production cost of peracetic acid can be reduced.



The method of the invention is now described in detail by way of examples. In the examples, brightness was measured in accordance with JIS P8123. The levels of addition of chemicals are expressed in weight % based on bone-dry pulp.

#### Example 1

Kraft process hardwood pulp (LKP) was used. This unbleached pulp had a brightness of 31.5% and a Kappa number of 12.4. The pulp was subjected to first-stage oxygen bleaching in an autoclave under the conditions of NaOH 3%,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  0.2%, pulp concentration 30%, max. temperature 100°C, oxygen pressure 6 kg/cm<sup>2</sup>, temperature increase over 90 min. and retention time 5 min. The treated pulp was diluted to 3% concentration, dehydrated to 25% and used as a substrate for peracetic acid bleaching. This pulp sample had a brightness of 46.1% and a Kappa number of 6.8. The pulp was then subjected to peracetic acid bleaching. The peracetic acid used was prepared by reacting acetic anhydride with hydrogen peroxide and had the composition of 45% peracetic acid, 11.5%  $\text{H}_2\text{O}_2$ , 20% acetic acid and 23.5% water. This peracetic acid bleaching was carried out under the following conditions. The results are set forth in Table 1.

1, a pretreatment was carried out. Thus, an acidic (sic) bleached pulp was diluted to a pulp concentration 8% and, for acid pretreatment, adjusted to pH 2 with 4N- $H_2SO_4$ . For treatment with a chelating agent, 0.1% of DTPA was added and the pH was adjusted to 7. In the case of phosphate treatment, 0.5% of sodium tripolyphosphate was added and the pH was adjusted to 8.

After either of the above pretreatments, the pulp was allowed to stand for 10 minutes and then dehydrated to 25%. These pulps were subjected to peracetic acid bleaching under the following conditions. The results are set forth in Table 3.

Table 3 Peracetic acid bleaching after pretreatment

Per- acetic acid $CH_3COOOH$ %	Con- comi- tant $H_2O_2$ %	$NaOH$ %	Pulp conc. %	Tempe- rature °C	Time hr	pH Be- fore/ after	% Consumption of chemical $CH_3COOOH$ $H_2O_2$	Bright- ness
<u>No pretreatment</u>								
5.0	1.28	5.0	15	70	2	7.4/5.4	99.9 23.6	73.2
<u>Pretreatment with acid</u>								
5.0	1.28	5.0	15	70	2	7.1/5.2	81.0 6.7	75.8
<u>Pretreatment with chelating agent</u>								
5.0	1.28	5.0	15	70	2	7.3/5.2	76.4 2.3	77.4
<u>Pretreatment with phosphate salt</u>								
5.0	1.28	5.0	15	70	2	7.4/5.3	80.4 5.1	76.1

Then, NaOH was added so as to activate the residual  $H_2O_2$  and hydrogen peroxide bleaching was performed. The results are shown in Table 4.

Table 4 Hydrogen peroxide post-bleaching

Residual $H_2O_2$ %	NaOH added %	Pulp conc. %	Tempe- rature °C	Time hr	pH Before/after	% Consumption of chemical	Bright- ness
<u>No pretreatment</u>							
0.98	1.5	13	70	2	11.1/9.7	97.3	80.8
<u>Pretreatment with acid</u>							
1.19	1.5	13	70	2	10.2/9.3	92.7	82.9
<u>Pretreatment with chelating agent</u>							
1.25	1.5	13	70	2	11.0/9.5	87.6	84.2
<u>Pretreatment with phosphate salt</u>							
1.22	1.5	13	70	2	11.0/9.7	91.2	83.5

It is apparent that these pretreatments helped reduce the consumption of chemicals and produce bleached pulps with improved brightness.

#### Example 3

Japanese fir wood RGP pulp was subjected to peracetic acid bleaching. This unbleached pulp had a brightness of 51.8%. After a pretreatment similar to that described in Example 2, the pulp was bleached with peracetic acid. The conditions and results are set forth in Table 5.

Then, NaOH was added and the bleaching process was

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